

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A233 732

PORT DATE

3. REPORT TYPE AND DATES COVERED

Reprint

4. TITLE AND SUBTITLE

Synthesis and Properties of
1,2-Difluorodinitroethylene

5. FUNDING NUMBERS

DAAL03-88-C-0013

6. AUTHOR(S) Kurt Baum, Thomas G. Archibald,
Dongjaw Tzeng, Richard Gilardi,
Judith L. Flippen-Anderson, and Clifford George

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Fluorochem, Inc. Laboratory for the Structure
680 S. Ayon Ave. of Matter
Azusa, CA 91702 Naval Research Laboratory
 Washington, D.C. 203758. PERFORMING ORGANIZATION
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-221110. SPONSORING/MONITORING
AGENCY REPORT NUMBER

ARO 25-761.1-CH

11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

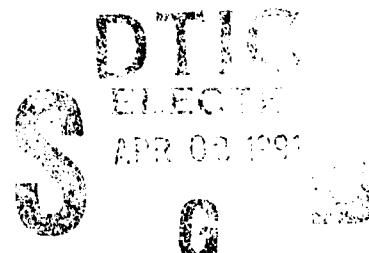
12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

1,2-Difluorodinitroethylene was synthesized by flash vacuum pyrolysis of 1,2-difluorotetranitroethane. X-ray crystallography showed that one of the two nitro groups is out of the plane of the rest of the molecule and that the C-C double-bond distance is unusually short at 1.284 Å. 1,2-Difluorotetranitroethane reacted with alcohols to give alkyl fluoronitroacetates and with anthracene and cyclopentadiene to give Diels-Alder adducts.



14. SUBJECT TERMS

nitro, fluorine, synthesis, crystallography

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

UL

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to *stay within the lines* to meet *optical scanning requirements*.

Block 1. Agency Use Only (Leave blank)

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered.

State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit
	Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number (If known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement.

Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."

DOE - See authorities.

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave blank.

DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.

NASA - Leave blank.

NTIS - Leave blank.

Block 13. Abstract. Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (*NTIS only*).

Blocks 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

Synthesis and Properties of 1,2-Difluorodinitroethylene

Kurt Baum,* Thomas G. Archibald, and Dongjaw Tzeng

Fluorochem, Inc., Azusa, California 91702

Richard Gilardi, Judith L. Flippen-Anderson, and Clifford George

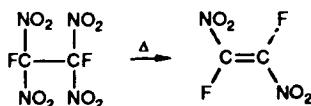
Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375

Received June 5, 1990

1,2-Difluorodinitroethylene was synthesized by flash vacuum pyrolysis of 1,2-difluorotetranitroethane. X-ray crystallography showed that one of the two nitro groups is out of the plane of the rest of the molecule and that the C-C double-bond distance is unusually short at 1.284 Å. 1,2-Difluorotetranitroethylene reacted with alcohols to give alkyl fluoronitroacetates and with anthracene and cyclopentadiene to give Diels-Alder adducts.

There has been recent interest in the effect of electro-negative substituents such as nitro¹ and fluorine² on the structural properties of olefins. Tetranitroethylene, the most electronegatively substituted olefin reported, is not sufficiently stable for convenient structural studies.³ This compound could be stored only under vacuum, apparently because small amounts of nitrogen oxide otherwise resulted in rapid autocatalytic decomposition. Tetranitroethylene was synthesized by the thermal extrusion of dinitrogen tetroxide from hexanitroethane. In the present study, this novel elimination reaction has been extended to the preparation of the more stable, fully substituted olefin, 1,2-difluorodinitroethylene.

1,2-Difluorotetranitroethane⁴ was prepared by the direct fluorination of the dipotassium salt of tetranitroethane in aqueous solution. Flash vacuum pyrolysis experiments were carried out on an apparatus similar to that described for the preparation of tetranitroethylene. Vaporized 1,2-difluorotetranitroethane was passed unchanged through a pyrolysis tube at 250 °C/0.5 mm. When the temperature was raised to 300 °C, approximately 25% of a new material was detected by ¹⁹F NMR. The vaporization of starting material to the combustion tube was slowed by cooling the material to 0 °C, and complete conversion was obtained. The product was identified as *trans*-1,2-difluorodinitroethylene and was isolated in 92% yield as a highly volatile solid. This olefin was stable to 105 °C, well above its melting point of 39–40 °C. Unlike tetranitroethylene, 1,2-difluorodinitroethylene could be handled under normal ambient conditions; it was only slightly hygroscopic and was storable indefinitely in a freezer.



X-ray crystallographic bond lengths and angles for *trans*-1,2-difluorodinitroethylene are shown in Table I, and the geometry is illustrated in Figure 1. One of the two nitro groups shows significant deviation from coplanarity with the rest of the molecule with the average value of the four torsion angles involving the C(1)-N(1) bond being

Table I. Bond Lengths (Å) and Angles (deg) for *trans*-1,2-Difluorodinitroethylene

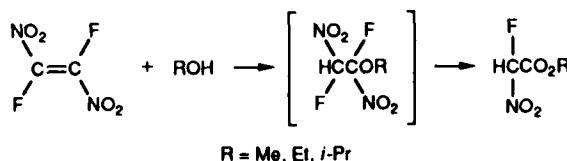
	Bond Length		
C(1)-F(1)	1.311 (5)	C(1)-N(1)	1.476 (5)
C(1)-C(2)	1.284 (6)	N(1)-O(1A)	1.206 (5)
N(1)-O(1B)	1.208 (5)	C(2)-F(2)	1.327 (5)
C(2)-N(2)	1.476 (5)	N(2)-O(2A)	1.208 (5)
N(2)-O(2B)	1.208 (5)		
	Bond Angle		
F(1)-C(1)-N(1)	113.2 (3)	F(1)-C(1)-C(2)	123.6 (4)
N(1)-C(1)-C(2)	123.2 (4)	C(1)-N(1)-O(1B)	119.8 (3)
C(1)-N(1)-O(1B)	114.2 (3)	O(1A)-N(1)-O(1A)	126.0 (3)
C(1)-C(2)-F(2)	122.6 (4)	C(1)-C(2)-N(2)	124.6 (4)
F(2)-C(2)-N(2)	112.8 (3)	O(2A)-N(2)-O(2B)	127.0 (3)
C(2)-N(2)-O(2B)	118.4 (3)	O(2A)-N(2)-C(2)	114.6 (3)

14.3°. Similar averaging gives 0.6° for the other nitro group and 0.8° for the C(1)-C(2) twist.

The C-N bond distances for both nitro groups are nearly identical (1.476 Å) and are similar to those reported for nitroethylene (1.45 Å). The C-C double-bond distance is unusually short at 1.284 Å. By comparison, the double-bond distance for tetracyanoethylene is 1.35 Å and that for tetrafluoroethylene, 1.311 Å.

The ¹³C NMR spectrum (Figure 2) is anomalous, showing a 2 × 2 × 3 pattern and unexplained signals centered at δ 144.5. The coupling constants are *J*_{CF} = 356.8, *J*_{CCF} = 77.5, and *J*_{CN} = 17.4 Hz. The area of the central signals is approximately the difference between that of the inner and outer triplets. The largest previously reported *J*_{CF} for a fluorolefin is 355 Hz for *trans*-dibromodifluoroethylene, and values of 200–300 are typical. The ¹⁹F NMR spectrum of the material showed only a singlet at δ -119.1, with no evidence of *cis*–*trans* isomers. The ¹⁴N NMR spectrum showed a singlet at δ -31.859.

The reaction of tetranitroethylene with alcohols to give alkyl dinitroacetates has been reported.³ The products were explained on the basis of the initial formation of the unstable tetranitroethyl ethers, which underwent loss of α-nitro groups. 1,2-Difluorodinitroethylene reacted similarly with methanol, ethanol, and 2-propanol to give the corresponding fluoronitroacetates, reported previously from reactions of the alcohols with fluoronitroacetyl chloride.⁵



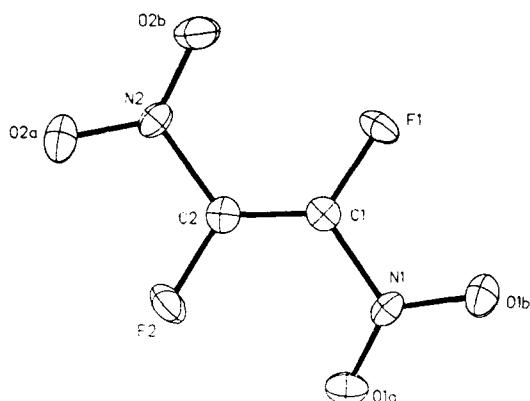
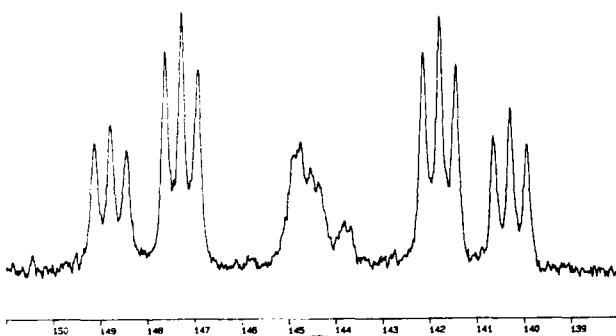
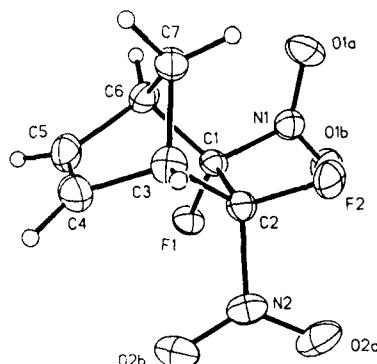
(1) Politzer, P.; Bar-Adon, R. *J. Am. Chem. Soc.* 1987, 109, 3529. Dewar, M. J. S.; Ritchie, J. P.; Alster, J. *J. Org. Chem.* 1985, 50, 1031. Penner, G. H. *J. Mol. Struct. (Theochem)* 1986, 137, 121–7.

(2) Smart, B. E. In *Molecular Structure and Energetics*, Vol. 3; Liebman, J. F., Greenberg, A., Eds.; UCH: Weinheim, Germany, 1986; pp 159–172. Carlos, J. L., Jr.; Karl, R. R. Jr.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* 1974, 70, 177–187.

(3) Baum, K.; Tzeng, D. *J. Org. Chem.* 1985, 50, 2736.

(4) Eremenko, L. T.; Natsubullin, F. Ya.; Borovinskaya, I. P.; Karpova, N. D. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1968, 431.

(5) Martynov, I. V.; Kruglyak, Yu. L. *Zh. Obshch. Khim.* 1965, 35, 967.

Figure 1. X-ray structure of *trans*-1,2-difluorodinitroethylene.Figure 2. ^{13}C NMR spectrum of *trans*-1,2-difluorodinitroethylene.Figure 3. X-ray structure of *endo*-5,exo-6-difluoro-5,6-dinitro-bicyclo[2.2.1]hept-2-ene.

Diels-Alder reactions of difluorodinitroethylene were also examined. Tetranitroethylene was previously shown to be an extremely reactive dienophile in Diels-Alder reactions, approximately an order of magnitude more reactive than tetracyanoethylene.³ Its reaction with anthracene was essentially instant at ambient temperature. By contrast, the reaction of 1,2-difluorodinitroethylene with anthracene in refluxing benzene was found to give a 47% yield in 4 h of the expected adduct, 11,12-difluoro-11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene, isolated as the benzene monosolvate. The reaction of 1,2-difluorodinitroethylene with cyclopentadiene at ambient temperature in methylene chloride gave *endo*-5,exo-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene in 49% yield. The crystallographic data and structure of this adduct are shown in Table II and Figure 3, respectively.

Experimental Section

Elemental analyses were obtained from Galbraith Laboratories. Melting points are uncorrected. ^1H and ^{19}F NMR spectra were

Table II. Bond Lengths (Å) and Angles (deg) for *endo*-5,exo-6-Difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene

Bond Length			
C(1)-F(1)	1.356 (5)	C(1)-N(1)	1.526 (6)
C(1)-C(2)	1.573 (6)	C(1)-C(6)	1.524 (6)
N(1)-O(1A)	1.207 (6)	N(1)-O(1B)	1.188 (5)
C(2)-F(2)	1.358 (5)	C(2)-N(2)	1.523 (6)
C(2)-C(3)	1.533 (6)	N(2)-O(2A)	1.200 (5)
N(2)-O(2B)	1.212 (6)	C(3)-C(4)	1.492 (7)
C(3)-C(7)	1.542 (7)	C(4)-C(5)	1.276 (8)
C(5)-C(6)	1.482 (7)	C(6)-C(7)	1.552 (7)
Bond Angle			
F(1)-C(1)-N(1)	104.4 (3)	F(1)-C(1)-C(2)	111.3 (3)
N(1)-C(1)-C(2)	109.3 (3)	F(1)-C(1)-C(6)	114.6 (3)
N(1)-C(1)-C(6)	114.1 (3)	C(2)-C(1)-C(6)	103.1 (3)
C(1)-N(1)-O(1A)	117.3 (4)	C(1)-N(1)-O(1B)	117.6 (4)
O(1A)-N(1)-O(1B)	125.1 (4)	C(1)-C(2)-F(2)	110.2 (3)
C(1)-C(2)-N(2)	110.4 (3)	F(2)-C(2)-N(2)	104.6 (3)
C(1)-C(2)-C(3)	102.5 (3)	F(2)-C(2)-C(3)	110.5 (4)
N(2)-C(2)-C(3)	118.6 (4)	C(2)-N(2)-O(2A)	117.2 (4)
C(2)-N(2)-O(2B)	116.6 (4)	O(2A)-N(2)-O(2B)	126.1 (4)
C(2)-C(3)-C(4)	107.5 (4)	C(2)-C(3)-C(7)	98.4 (3)
C(4)-C(3)-C(7)	98.9 (4)	C(3)-C(4)-C(5)	109.4 (5)
C(4)-C(5)-C(6)	109.2 (5)	C(1)-C(6)-C(5)	103.3 (4)
C(1)-C(6)-C(7)	101.2 (3)	C(5)-C(6)-C(7)	99.0 (4)
C(3)-C(7)-C(6)	93.8 (4)		

obtained on a Varian T-60 spectrometer and ^{13}C NMR spectra on a Bruker AC200 spectrometer in CDCl_3 . Chemical shifts are in ppm relative to TMS or FCCl_3 . IR spectra were obtained in CH_2Cl_2 on a Perkin-Elmer 700 spectrometer. *Polynitro compounds are potentially explosive and proper shielding should be used.*

trans-1,2-Difluorodinitroethylene. A 10-mL flask containing 1,2-difluorotetranitroethane (1.58 g, 6.42 mmol) was connected in series to a horizontal 1.25 cm \times 45 cm quartz tube, two traps, and a vacuum system. The flask and traps were cooled with baths at 0 °C, -20 °C, and -78 °C, respectively, the quartz tube was heated at 300 °C with a tube furnace, and the system was evacuated to 0.5 mmHg. After 20 min the starting material had evaporated. The system was vented to the atmosphere, and the -20 °C trap was warmed to ambient temperature to allow evaporation of a small amount of N_2O_4 . This trap was found to contain 0.91 g (92%) of *trans*-1,2-difluorodinitroethylene, a highly volatile, pale yellow solid, mp (DSC) 39–40 °C sub, 105 °C dec: IR 1575, 1340, 950 cm⁻¹; ^{13}C NMR δ 146.1 (2 \times 2 \times 3, J = 356.8, 77.5, 17.4 Hz and asym multiplet at 144.5); ^{19}F NMR δ -119.1 (s, 17 Hz at $1/2$ height); ^{14}N NMR δ -31.86 (s, 10 Hz at $1/2$ height). Anal. Calcd for $\text{C}_2\text{F}_2\text{N}_2\text{O}_4$: C, 15.59; F, 24.67. Found: C, 15.43; F, 24.47.

Isopropyl Fluoronitroacetate. A solution of 1,2-difluorodinitroethylene (1.42 g, 9.22 mmol) in 2-propanol (100 mL) was refluxed for 3 h. The solvent was evaporated and the residue distilled to give 0.38 g (25%) of isopropyl fluoronitroacetate, bp 87–89 °C (42 mmHg) [lit.⁵ 72 °C (9 mm)]: IR (CCl_4) 1720, 1590 cm⁻¹; ^1H NMR δ 5.90 (d, J = 46 Hz, 1 H), 5.15 (sept, 1 H, J = 6 Hz), 1.38 (d, 6 H, J = 6 Hz); ^{19}F NMR δ -140.5 (d, J = 46 Hz). Anal. Calcd for $\text{C}_5\text{H}_8\text{FNO}_4$: C, 36.37; H, 4.88; F, 11.51; N, 8.48. Found: C, 36.31; H, 4.87; F, 11.64; N, 8.25.

Ethyl Fluoronitroacetate. The reaction of 1,2-difluorodinitroethylene (0.807 g, 5.24 mmol) with ethanol (100 mL) by the above procedure gave ethyl fluoronitroacetate (0.273 g, 34.5%), bp 85 °C [lit.⁵ 74 °C (12 mmHg)]: IR (CCl_4) 1725, 1590 cm⁻¹; ^1H NMR δ 1.2 (t, J = 7 Hz, 3 H), 3.7 (q, 2 H, J = 7 Hz), 5.80 (d, 1 H, J = 46 Hz); ^{19}F NMR δ -144 (d, J = 46 Hz).

Methyl Fluoronitroacetate. The reaction of 1,2-difluorodinitroethylene (0.788 g, 5.12 mmol) with methanol (100 mL) by the above procedure gave methyl fluoronitroacetate (0.202 g, 29%), bp 88–92 °C [lit.⁵ 85 °C (30 mmHg)]: IR (CCl_4) 1720, 1590 cm⁻¹; ^1H NMR δ 4.0 (s, 3 H), 6.15 (d, 1 H, J = 46 Hz); ^{19}F NMR δ -144 (d, J = 46 Hz).

11,12-Difluoro-11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene. A solution of 1,2-difluorodinitroethylene (0.080 g, 0.52 mmol) and anthracene (0.200 g, 1.12 mmol) in benzene (12 mL) was refluxed for 4 h and cooled to room temperature. A white solid separated and was recrystallized from benzene to give 0.099 g (47%) of 11,12-difluoro-11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene benzene monosolvate, mp 192–193 °C: IR 1590,

1350 cm^{-1} ; ^1H NMR δ 7.2 (m, 14 H), 4.9 (m, 2 H); ^{19}F NMR δ -121.5 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_4$: C, 64.39; H, 3.93; F, 9.26; N, 6.82. Found: C, 64.14; H, 4.09; F, 9.18; N, 6.96.

endo-5,exo-6-Difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene.
 A solution of 1,2-difluorodinitroethylene (0.299 g, 1.94 mmol) and freshly distilled cyclopentadiene (1.5 g, 23 mmol) in CH_2Cl_2 (10 mL) was stirred under nitrogen for 10 min at ambient temperature. The solvent was evaporated and the residual oil was chromatographed (silica gel, CH_2Cl_2) to give 0.209 g (49%) of *endo*-5,exo-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene, mp 81–82 °C: IR 1560, 1320 cm^{-1} ; ^1H NMR δ 6.6 (m, 1 H), 6.3 (m, 1 H), 3.5 (m, 2 H), 2.6 (m, 1 H), 2.3 (m, 1 H); ^{19}F NMR δ -121.03 (bs). Anal. Calcd for $\text{C}_7\text{H}_8\text{F}_2\text{N}_2\text{O}_4$: C, 38.19; H, 2.75; F, 17.26. Found: C, 38.20; H, 2.89; F, 16.98.

X-ray analysis of *trans*-1,2-difluorodinitroethylene: $C_2F_2N_2O_4$, $M_r = 154.0$, orthorhombic space group $Pbca$, $a = 9.375$ (2), $b = 0.122$ (3), and $c = 10.505$ (3) Å, $V = 996.8$ (4) Å 3 , $Z = 8$, $D_X = 2.053$ Mg m $^{-3}$, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.22$ mm $^{-1}$, $F(000) = 608$, data collection $T = 201$ K, final $R = 0.055$, $wR = 0.066$ for 578 independent reflections with $F_0 > 3\sigma(F_0)$.

A clear colorless $0.01 \times 0.42 \times 0.51$ mm crystal grown by sublimation was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator, and 20 centered reflections within $22 < 2\theta < 39^\circ$ were used for determining lattice parameters. ($\sin(\theta)/\lambda_{\max} = 0.54 \text{ \AA}^{-1}$; range of hkl , $-10 \leq h \leq 10$, $0 \leq k \leq 10$, and $0 \leq l \leq 11$). Standard reflections 400, 040, 004 monitored every 100 reflections with random variations up to $\pm 2.5\%$ over data collection, θ/θ inode, scan width $[2\theta(K_{\alpha 1}) - 0.9^\circ]$ to $[2\theta(K_{\alpha 2}) + 0.9^\circ]$, 2θ scan rate $60.0^\circ \text{ min}^{-1}$ (rapid due to volatile crystal); 1534 reflections measured, 654 unique, 587 observed with $F_o > 3\sigma(F_o)$; $R_{\text{int}} = 0.042$. Data was corrected for Lorentz and polarization, but not absorption effects. Structure was solved by direct methods. The least-squares refinement minimized the quantity $\sum w(|F_{\text{ol}}| - |F_{\text{cl}}|)^2$, where $w = 1/[c^2(|F_{\text{ol}}|) + g(|F_{\text{ol}}|)^2]$, $g = 0.00023$. Secondary extinction parameter $p = 0.0029(8)$ in F_{c}^{2m} $F_{\text{c}} = F_{\text{o}}/[1.0 + 0.002(p)F_{\text{o}}^2/\sin(2\theta)]^{0.25}$. There were 92 parameters refined: all atom coordinates, anisotropic temperature parameters for nonhydrogen atoms; the hydrogen atoms were assigned fixed isotropic thermal parameters. ($\Delta/\sigma)_{\max} = 0.01$, $R = 0.055$, $wR = 0.066$, $S = 2.88$. Final difference Fourier excursions 0.51 and -0.28 \AA^{-3} . Atomic scattering factors from *International Tables for Crystallography*.⁶ The programs used for structure solution, refining, and plotting are part of SHELXTL.^{7,8}

(6) *International Tables for X-ray Crystallography*, Vol. IV; Kynoch Press: Birmingham, England, 1974 (present distributor D. Reidel, Dordrecht).

X-ray analysis of *endo*-5,ex_o-6-difluoro-5,6-dinitro-bicyclo[2.2.1]hept-2-ene: $C_7H_6F_2N_2O_4$, $M_r = 220.14$, orthorhombic space group $P22_12_1$, $a = 6.033$ (3), $b = 11.629$ (4), and $c = 12.501$ (4) Å, $V = 877.1$ (3) Å³, $Z = 4$, $D_X = 1.667$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.54183$ Å, $\mu = 1.42$ mm⁻¹, $F(000) = 448$, data collection $T = 295$ K, final $R = 0.045$, $wR = 0.047$ for 736 independent reflections with $F_o > 3\sigma(F_o)$.

A clear colorless $0.05 \times 0.40 \times 0.25$ mm crystal recrystallized from carbon tetrachloride was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator; 25 centered reflections within $45 < 2\sigma < 88^\circ$ were used for determining lattice parameters. ($\sin(\theta)/\lambda$)_{max} = 0.56 Å⁻¹; range of hkl , $0 \leq h \leq 6$, $0 \leq k \leq 13$, and $0 \leq l \leq 14$. Standard reflections 400, 040, 006 monitored every 100 reflections showed a linear decay of $\pm 15\%$ over data collection, $\theta/2\theta$ mode, scan width [$2\theta(K_{a1}) - 1.0$] to [$2\theta(K_{a2}) + 1.0$] $^\circ$, 2σ scan rate 60° min⁻¹ (rapid due to volatile crystal, full data set collected in 4 h); 855 reflections measured, 841 unique, 736 observed with $F_o > 3\sigma(F_o)$; $R_{\text{int}} = 0.030$. Data was corrected for Lorentz and polarization, and an empirical absorption correction was applied. The maximum and minimum transmission values were 0.77 and 0.72. Structure was solved by direct methods. The least-squares refinement minimized the quantity $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(|F_o|) + g \cdot (F_o)^2]$, $g = 0.00023$. Secondary extinction parameter $p = 0.012 (1)$ in $F_c^* = F_c/[1.0 + 0.002(p)F_c^2/\sin(2\sigma)]^{0.25}$. There were 137 parameters refined: atom coordinates and anisotropic temperature parameters for non-hydrogen atoms; the hydrogen atoms riding on covalently bonded carbon atoms (C–H distance set at 0.96 Å and angles involving H atoms idealized at tetrahedral or trigonal values, as appropriate. (Δ/σ)_{max} = 0.04, $R = 0.045$, $wR = 0.047$, $S = 1.41$. Final difference Fourier excursions 0.16 and -0.18 e Å⁻³. Atomic scattering factors from *International Tables for Crystallography*.⁶ The programs used for structure solution, refining, and plotting are part of SHELLXTL.^{7,8}

Acknowledgment. This work was supported by the U.S. Army Research Office and the Office of Naval Research, Mechanics Division. We thank Dr. M. Coburn of Los Alamos National Laboratory for the ^{14}N NMR spectrum.

(7) Sheldrick, G. M. "SHELXTL80, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data", University of Göttingen, Federal Republic of Germany, 1980.

(8) Tables of atom coordinates, bond distances and angles, structure factors, anisotropic thermal parameters, and hydrogen coordinates are included in the supplementary material.

A-1 20